procedure given in ref. 4a. All reactions were performed in a stock solution similar to one previously used.[7,14] This solution was prepared by combining 700 ml. of redistilled glacial acetic acid, 166.4 ml. of redistilled hydrobromic acid, and 43.6 ml. of redistilled water. The ketone concentration was 500×10^{-5} *M*. The results are summarized in Table II.

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(14) F. A. Vingiello, J. G. Van Oot, and H. H. Hannabass, *J. Am. Chem. Soc.*, **74**, 4546 (1952).

Comments on N.m.r. Spectra of Some Optically Active Dimethylcyclohexenes

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We had occasion to prepare three isomeric optically active dimethylcyclohexenes: (+)-2,4-dimethylcyclohexene, (+)-1,3-dimethylcyclohexene, and (−)-3-methylmethylenecyclohexane. Confusion surrounded their identities, but we offer absolute proof of structure, n.m.r. proof which discloses methyl group positions on cyclohexene.

Experimental

(+)-3-Methylcyclohexanone was prepared by the method of Djerassi and Krakower[1] from pulegone (Eastman, $[\alpha]^{29}\mathrm{D}$ +23.49). A portion of the product was purified ($[\alpha]^{25}\mathrm{D}$ +13.09); the bulk, 0.815 mole, was dried, dissolved in 300 ml. of ether, and added dropwise to 1.23 moles of methylmagnesium iodide in 325 ml. of ether. After being stirred overnight the Grignard complex was decomposed as described. A distillation head was fitted to the reaction vessel and 100 ml. of 50 vol. % aqueous sulfuric acid was added with stirring over a period of 1.5 hr.[2]; immediately following addition of acid, 550 ml. of water was added with cooling and the olefin mixture was steam distilled.[3] The mixture, which contains 60% 2,4-, 38% 1,3-, and 2% *exo*-olefin, was separated by repeated fractionations through a 90 × 0.5 cm. spinning band column (Podbieliniak). On the basis of rated plates of the column[4] and compositions of several fractions we estimate the difference in boiling points between (+)-2,4-dimethylcyclohexene and (+)-1,3-dimethylcyclohexene to be less than 1° and probably less than 0.5°; we detected no difference in boiling points during fractionation, but gas chromatographic analyses of distillation fractions revealed the 2,4-olefin to be higher boiling. All analyses were done on a 73 ft. × 0.25 in. LAC-446 on firebrick (20% by weight) gas–liquid chromatographic column (Aerograph) from which the olefins emerge in the order: *exo*-; 1,3-; 2,4-. Table I compares some new and old physical constants.

Proton magnetic resonance spectra of the olefins were obtained with an A-60 n.m.r. spectrometer (Varian Associates); pertinent information is shown in Table II.

TABLE I

SOME PHYSICAL CONSTANTS OF THE CYCLOOLEFINS

Olefin	n_{D}	Temp., °C.	d_4	Temp., °C.	B.p., °C.	Press.	[α]	λ	Temp., °C.	Ref.
2,4-Dimethylcyclohexene	1.4442	25.5	0.802	25	130–1	750	+135.16	589	29	[a]
	1.4467	25	.803	25	129	. . .	+112.90	579	25	[b]
	1.446	25	.801	25	128	760	Racemic			[c]
	1.4448	25	.806	27	124.5–125	719	+ 91.4	589	27	[d]
	1.4518	20	. . .	. . .	127–129	. . .	Racemic			[e]
1,3-Dimethylcyclohexene	1.4465	25.5	.799	25	130–131	750	+ 34.20	589	29	[a]
	1.4480	25	.807	25	127	. . .	+ 65.36	579	25	[b]
	1.443	25	.798	25	137	760	Racemic			[c]
	1.4493	20	.805	20	124.5	740	Racemic			[f]
	. . .	. . .	. . .	. . .	124–129	758	Racemic			[g]
3-Methylmethylenecyclohexane	1.4429	25.5	.783	25	121	750	− 45.93	589	29	[a]
	1.4434	25	.791	25	120.5	. . .	− 49.32	579	25	[b]

[a] This work; rotations of pure olefins were calculated from rotations and compositions of various binary mixtures assuming rotations are additive. For purities of samples, see Table II. [b] M. Mousseron, R. Richard, and R. Granger, *Bull. soc. chim. France*, **13**, 222 (1946). [c] "Physical Properties of Chemical Compounds," Vol. 1, R. R. Dreisbach, Ed., American Chemical Society, Washington, D. C., 1955, pp. 497, 499. [d] S. Siegel and M. Dunkel, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1956, p. 15. [e] J. Meinwald and R. F. Grossman, *J. Am. Chem. Soc.*, **78**, 992 (1956). [f] J. E. Nickels and W. Heintzelman, *J. Org. Chem.*, **15**, 1142 (1950). [g] K. W. Rosennund, H. Herzberg, and H. Schutt, *Ber.*, **87**, 1258 (1954).

Discussion

Optical rotations of our 2,4- and 1,3-olefins differ considerably from previous reports. We believe this arises from different methods of establishing purity and not from racemization; *e.g.*, our 2,4-olefin has higher and our 1,3-olefin *lower* rotation than previously reported samples. We were able to establish compositions of mixtures by gas–liquid chromatography, an analytical tool not available to former workers. Because of their close boiling points, mixtures of these two olefins appear never to have been separated.

The proton magnetic resonance spectra offer absolute proof of methyl group position on cyclohexene rings Olefinic protons absorb in the usual region with exocyclic olefinic protons somewhat upfield.[5] Methyl bands occur around 91 and 50 c.p.s. Since those at 91 c.p.s. are less shielded and not split, they are attached to sp^2 hybridized carbons. Those at 50 c.p.s. are split into two peaks, the upfield one being less intense. In our case no ambiquity arises because comparison of the three spectra clearly reveals identical splitting of the 50-c.p.s. peaks of (+)-2,4-dimethylcyclohexene and

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(1) C. Djerassi and G. W. Krakower, *J. Am. Chem. Soc.*, **81**, 241 (1959).

(2) While sulfuric acid is being added, ether distils and must be replenished from time to time to maintain low viscosity and low temperature.

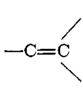
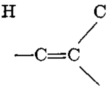
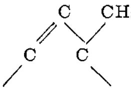
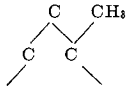
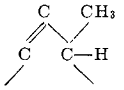
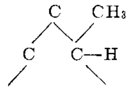
(3) Olefin removal temperature is critical; in previous preparations racemates were obtained when distillation temperature rose above 100°.

(4) "Technique of Organic Chemistry," Vol. IV, A. Weissberger, Ed. Interscience Publishers, Inc., New York, N. Y., 1961, p. 169.

(5) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959 p. 61.

Table II

Some Pertinent N.M.R. Data of the Cycloolefins

			Chemical shifts (c.p.s.)[a]				Spin–spin splittings[b]	
	Purity[c]	Impurity						
(+)-2,4-Dimethylcyclohexene	90.6	1,3-	314[d]	91	..	51	..	5.4
(+)-1,3-Dimethylcyclohexene	91.8	2,4-	308[d]	92	52	..	7.0	...
(−)-3-Methylmethylenecyclohexane	98.4	1,3-	268[e]	..	..	48	...	5.4

[a] Spectra obtained on scale of 500 c.p.s.; external standard of tetramethylsilane; error is about ±2 c.p.s. [b] Spectra obtained on scale of 100 c.p.s.; error is ±0.2 c.p.s.—this is X-part of typical AX_3 type system, A-part is buried in envelope caused by protons attached to ring. [c] Purer fractions were not of sufficient volume for obtaining n.m.r. data. [d] Integrated areas show one proton. [e] Integrated areas show two protons.

(−)-3-methylmethylenecyclohexane. This fact coupled with different splitting of the 50-c.p.s. peaks of (+)-2,4-dimethylcyclohexene and (+)-1,3-dimethylcyclohexene establishes the relative structures; *i.e.*, the 2,4-olefin has one methyl similar to the one on the *exo*-olefin but the 1,3-olefin does not.

There is a more fundamental means of deciding which spectra represents the 1,3- and which represents the 2,4-olefin other than merely comparing the spectra with that of the *exo*-olefin. The methyl doublets around 50 c.p.s. appear at first glance to be B-parts of typical AB_3 spectra; however, the difference in chemical shifts (δ) between the tertiary proton and the methyl group is large enough in each case (*i.e.*, $J/\delta < 0.25$) to be considered AX_3 systems, and both methyl groups should be sharp doublets.[6,7] This is the case for the 1,3-olefin, but for the 2,4-olefin the doublet is not so well resolved and a shoulder is present on the upfield side of the less intense member. Therefore, these splitting patterns should be interpreted along the lines suggested by Anet[8] to explain the splittings of the methyl groups of certain 6α- and 6β-methyl steroids. The tertiary proton is coupled to protons on carbons adjacent to it in the ring and, even though these adjacent protons do not split the methyl protons, they influence the splitting between the tertiary proton and the methyl protons. This secondary effect is minimized when the ratio J/δ between the tertiary proton and adjacent ring protons becomes less than 0.5.[8] Our data are in agreement with this explanation, for when the tertiary proton is allylic and shifted away from the ring protons as in the 1,3-olefin, the methyl group doublet at 50 c.p.s. is split to the base line. However, when the tertiary proton and the adjacent ring protons have very nearly the same chemical shift as in the 2,4- and *exo*-olefin, the doublet is poorly resolved and appears to contain some lines between the two major lines.

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[6] See ref. 5, p. 95.

[7] K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 301.

[8] F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961).

Synthesis and Identification of Dispiro[5.1.5.1]tetradecane[1]

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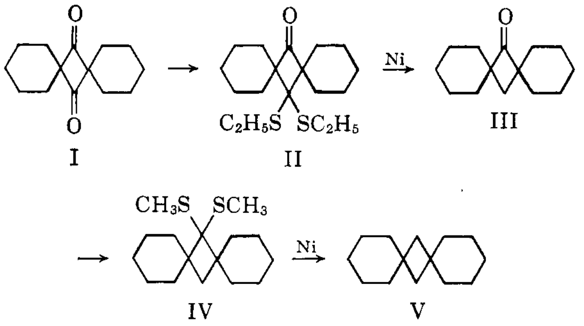
Walborsky and Buchman[2] reported the synthesis of dispiro[5.1.5.1]tetradecane from cyclohexyl ketene dimer according to the following reaction sequence.



An attempt to reproduce their work led to the isolation of compounds IV and V in higher yields than they reported and with different physical properties. Chemical and instrumental evidence are presented to show that the hydrocarbon of properties described in this work is dispiro[5.1.5.1]tetradecane.

The attempt to reproduce Walborsky and Buchman's work gave results in reasonable agreement with those reported through compound III, dispiro[5.1.5.1]tetradecan-7-one. However, the dithioketal (IV) was obtained in 76% yield as a solid melting at 117–119°, while Walborsky and Buchman reported a 48% yield of a solid melting at 83.5–84.5°. Dispirotetradecane (V) was obtained in 86% yield as a solid melting at 56.5–58°, rather than the reported 17% yield of a liquid boiling at 131° (10 mm.), m.p. 10°.

Several other approaches to the synthesis were attempted. Buchman and Herzog[3] earlier reported a successful Wolff–Kishner reduction of the disemicar-

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[1] This work was presented before the Division of Organic Chemistry at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

[2] H. M. Walborsky and E. R. Buchman, *J. Am. Chem. Soc.*, **75**, 6339 (1953).